

# Orbital moment of a single Co atom on a Pt(111) surface - a view from correlated band theory.

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**Abstract.** The orbital magnetic moment of a Co adatom on a Pt(111) surface is calculated in good agreement with experimental data making use of the LSDA+U method. It is shown that both electron correlation induced orbital polarization and structural relaxation play essential roles in orbital moment formation. The microscopic origins of the orbital moment enhancement are discussed.

## 1. Introduction.

According to Hund's rules, gas-phase transition metal atoms possess large spin  $M_S$  and orbital  $M_L$  moments mediated by intra-atomic Coulomb interactions. In a solid, where electron delocalization and crystal field effects compete with Coulomb interactions, there is a substantial decrease in  $M_S$  and partial or total quenching of  $M_L$ .

Recent X-ray magnetic circular dichroism (XMCD) measurements [1] report  $M_S$  and  $M_L$  of Co-atom and small Co clusters on Pt(111) in an ultra-high-vacuum. The  $M_L = 1.1 \pm 0.1 \mu_B$  and  $M_S + 7M_D = 1.8 \pm 0.1 \mu_B$  (where  $M_D$  is a spin dipole moment) were evaluated from XMCD spectra using the conventional sum rules [2]. The number of holes in the Co atom 3d-manifold  $n_d=2.4$  was taken from local spin-density calculations (LSDA). The XMCD experiments are complimented by spin-polarized-relativistic Korringa-Kohn-Rostocker (KKR) Greens function LSDA theoretical calculations, and  $M_S = 2.14 \mu_B$  and  $M_L=0.60 \mu_B$  for Co site were obtained. No structural relaxation of the Co atom position over the Pt surface was considered, and the atomic-sphere approximation was employed.

The authors of Ref.[1] assumed that the  $M_L$  discrepancy between the KKR-LSDA theory and the XMCD experiments originates from the lack of orbital polarization (OP) in LSDA. They used the well known orbital polarization correction of Brooks [3], adding to the LSDA total energy functional an *ad-hoc* term  $\frac{1}{2}B_R M_L^2$  with the LSDA calculated Racah parameter  $B_R$ . This form of OP correction was widely used in the past to improve upon  $M_L$  in the bulk transition *d*- and *f*-metals where sometimes it works well [4].

For the Co-atom on Pt surface, Gambardella *et al.* found out that the Brooks OP yields the  $M_L$  which substantially exceeds the experimental value. They had to reduce the LSDA calculated  $B_R$  by 50 % in order to obtain a  $M_L=1.50 \mu_B$  comparable with the experimental XMCD data. It is assumed in [1] that the reduction of  $B_R$  compensates for a lack of structural relaxation.

In this work we explore another avenue for the orbital polarization correction to LSDA which is based on the correlated band theory LSDA+U method [5]. It consists of LSDA augmented by a correcting energy of a multiband Hubbard type and a "double-counting" subtraction term which accounts approximately for an electron-electron interaction energy already included in the LSDA. Minimization of the LSDA+U functional generates not only the ground state total energy, but also one-electron band structure energies and spin-orbital states. The basic difference between LSDA+U method and the LSDA is its explicit dependence on on-site spin and orbitally resolved occupation matrices. The LSDA+U method creates in addition to the spin-only dependent LSDA potential, the spin and orbitally dependent on-site "+U" potential which gives OP beyond that given by the LSDA (where it comes from the spin-orbit coupling only).

It was shown by Solovyev *et al.* [6] that LSDA+U produces the correct OP for insulating 3d-oxides. Recent parameter-free GW calculations for transition metal based materials [7] produce OP which is very similar to LSDA+U results with the appropriate choice of Coulomb- $U$  [8].

## 2. Results and Discussion.

We performed supercell calculations to model a Co adatom at a Pt(111) surface. The supercell consists of three Pt(111) layers with doubled (p(2x2)) 2-dimensional unit

cell, and the Co atom on the top taken in the *fcc* position (see Fig. 1). The vacuum is modeled by the equivalent of two empty Pt layers. All in-plane inter-atomic distances are adopted to be those of pure Pt. The distance between the Co atom and the Pt surface was varied in the calculations. We note that while the chosen supercell is quite small, it provides separation of Co atoms beyond the second nearest neighbors distance and includes interaction of Co with first and second Pt nearest neighbors. Herein, we assume that the given supercell is sufficient for Co  $M_L$  calculations, which is mainly a local quantity.

We use the LSDA+U method implemented in the full-potential linearized augmented plane-wave (FP-LAPW) method including spin-orbit coupling (SOC) [9, 16]. When SOC is taken into account, the spin is no longer a good quantum number, and the LSDA+U total-energy functional contains additional spin-off-diagonal elements of the on-site occupation matrix  $n_{m_1\sigma_1, m_2\sigma_2}$  [6]. The LSDA contributions to the effective potential (and corresponding terms in the total energy) are corrected to exclude the non-spherical interaction. It helps to avoid the *d*-states non-spherical Coulomb and exchange energy “double counting” of *d*-states in LSDA and “+U” parts of the effective potential and also corrects the non-spherical self-interaction of the *d*-states.

In the self-consistent calculations we used 48 special *k*-points in combination with a Gaussian smearing for the *k*-point weighting. A quasi-2D Brillouin zone (BZ) with  $k_z = 0$  was adopted in order to simulate the 2D-character of the problem, notwithstanding that the supercell calculations themselves are inherently three dimensional. The “muffin-tin” radii used are  $R_{MT} = 2.2$  a.u. for Co and 2.5 a.u. for Pt and  $R_{MT}^{Co} \times K_{max} = 7.7$ , with  $K_{max}$  the cut-off for the LAPW basis. The Coulomb- $U=2$  eV and exchange- $J=0.9$  eV were chosen which are in the range of commonly accepted values for 3*d*-metals. In principle,  $U$  can be calculated by linear-response LSDA procedure [11] or from GW [7], both yielding the values  $\sim 2$  eV. As for exchange- $J$ , it is not affected by solid-state screening and equal to LSDA calculated Stoner exchange parameter. The spin quantization axis is fixed along the out-of-plane *z*-direction.

First let us make a comparison with the results of KKR for unrelaxed geometry (see Table I.). The LSDA calculated values of  $M_S$  and  $M_L$  agree quite well. However, the  $M_L$  per *d*-hole is somewhat bigger in KKR than in FP-LAPW calculations since *d*-shell occupation is bigger in KKR (7.6) than in FP-LAPW (7.2). It is probably due to the difference in the radius of ASA-spheres used in KKR and MT-radius in FP-LAPW. Since in KKR calculations [1] they use the same radius for ASA-sphere for the “big” Pt-atom and the “smaller” Co-atom, this difference can become significant and affect both the charge and spin density distributions.

The XMCD experiments measure not the  $M_L$  itself but the  $M_L$  per *d*-hole ratio  $M_L/n_h$ . The  $M_L/n_h$  calculated in KKR and FP-LAPW for unrelaxed geometry and making use of LSDA is a factor of two smaller than one measured by XMCD. It was already mentioned above that Ref.[1] proposed the use of the Brooks OP with reduced  $B_R$  in order to improve the agreement with experimental data. Here we show that the  $B_R$  reduction alone does not solve the problem. Rather it attempts to compensate for limitations of the calculations without taking account of structural relaxation in open systems including an important class of 3*d*-adatoms and clusters.

Next, we turn to the salient aspect of our investigation, the LSDA+U calculations. When the Co-Pt inter-atomic distance as for pure Pt is used, the calculated  $M_L$  and  $M_L/n_h$  are quite big (see Table I.). By varying  $d_{Co-Pt}$  and minimizing the total

energy we find the equilibrium  $d_{Co-Pt} \approx 3.48$  a.u., i.e. reduced by almost 20 %. Since we do not perform a full relaxation and the amount of Pt in our supercell is relatively small, we can not claim that this will be the correctly optimized  $d_{Co-Pt}$ . Nevertheless it is reasonable to assume that calculated  $d_{Co-Pt}$  distance is approximately correct [12].

The change in  $d_{Co-Pt}$  has strong effect on  $M_L$  and  $M_L/n_h$  (shown in Table I.). The  $M_L/n_h$  becomes fairly close to the experimental value and the agreement for  $M_L$  is also substantially improved. We should keep in mind that the “experimental” value is given as a product of measured  $M_L/n_h$ -ratio times the KKR-calculated  $n_h$  of 2.4. Making use of the LSDA+U calculated  $n_h=2.9$ , we obtain the “experimental”  $M_L$  of  $1.34 \pm 0.12 \mu_B$ , which is in good agreement with the LSDA+U calculated value.

To understand how the enlargement of the Co  $M_L$  in the LSDA+U approach comes about we consider the spin and orbitally resolved 3d densities of states ( $dDOS$ ), which are shown in Fig. 2. The spin-resolved  $dDOS$  (see Fig. 2(a)) reveals a substantial narrowing of the band width from  $\sim 6$  eV for hcp Co to  $\sim 4$  eV for the Co ad-atom as well as a moderate increase in the spin-splitting, as is expected for the reduced Co coordination. The spin-down DOS is split at the vicinity of  $E_F$ . When  $dDOS$  is resolved in terms of cubic harmonics (see Fig. 2(b)), it becomes clear that the spin-down peak below  $E_F$  possesses  $e_g : 3z^2 - r^2$ -orbital character while the spin minority d-holes are of  $e_g : x^2 - y^2$  and  $t_{2g}$ -orbital character.

Since the spin-up Co  $d$ -band is fully occupied, only changes of the spin-down band are essential for the  $M_L$  enhancement. The  $m_l$ -resolved Co- $dDOS$  is shown in Fig. 2(c) for the spin-up and spin-down channels. The major contribution to the increase of  $M_L$  originates from  $|m_s = -\frac{1}{2}; m_l = +2\rangle$  orbital. The  $M_L$  enhancement is brought about by in-plane spin-down  $x^2 - y^2$  and  $xy$  orbitals and much less affected by out-of-plane  $xz, yz$  orbitals. The spin-down  $3z^2 - r^2 (\sim |m_l = 0\rangle)$  orbital does not contribute to  $M_L$ . This out-of-plane  $3z^2 - r^2$  orbital is the most localized due to the smallest overlap between Co-3d and Pt-5d electrons.

It is necessary to mention that our analysis can not be regarded as truly *ab-initio* due to the use of external Coulomb- $U$ . Herein we make use of a “commonly used” value of  $U=2$  eV while it can be at least in principle obtained from constrained LSDA calculations [11]. With increase of  $U$  the  $M_L$  value will increase, and with decrease of  $U$  it will decrease. Nevertheless our results show quantitatively the role of Coulomb- $U$  in the  $M_L$  formation.

Also, we did not consider here the magneto-crystalline anisotropy (MAE) induced by Co-adatom. In contrast to  $M_L$  which is mostly a local property of the Co atom, the MAE will consist of contributions from the Co atom as well as the Pt neighbors due to strong Pt atom SOC [8]. Most probably, the quantitative studies of the MAE will require a bigger supercell; this is the subject of further work.

Still we can make a rough estimate for the contribution of the Co adatom into the MAE. When spin is rotated from the z-axis (out-of-plane) to the x-axis (in-plane) direction there is only a little change in the value of the Co atom  $M_S$ , from  $2.14 \mu_B$  (z-axis) to  $2.16 \mu_B$  (x-axis). The change in  $M_L$  is substantially greater, from  $1.58 \mu_B$  (z-axis) to  $1.42 \mu_B$  (x-axis). Indeed, this strong anisotropy in  $M_L$  paves the way for the strong MAE. Qualitatively, the Co atom contribution to the MAE can be estimated making use of Bruno’s relation [13]  $MAE = (E_x - E_z) \approx -\xi/4(M_L^x - M_L^z)$ , where  $\xi$  is the SOC constant (76 meV for Co-adatom). In the LSDA+U calculations, we obtain the MAE of  $\approx 3.2$  meV/Co which is somewhat smaller than the experimental value of  $9.3 \pm 1.6$  meV. A similar estimate for the LSDA calculations yields the MAE of  $\sim 2.0$

meV/Co. While our estimate gives the MAE which is smaller than the experimental data, it is exceptionally large compared with other Co-based materials: a few tenth of meV for Co/Pt and Co/Au multilayers, and 2.0 meV for Co monatomic wire [14].

We note that the orbital moment enhancement has been recently investigated in Ref. [14] for the case of the Co monatomic wire on the Pt(111) surface step edge. Making use of XMCD the experimental value of the Co atom  $M_L = 0.68 \pm 0.05 \mu_B$  was found, which is somewhat smaller than for the Co adatom case. Also, it was shown that LSDA yields the Co monatomic wire  $M_L \sim 0.16 \mu_B$  which is substantially smaller than the XMCD experimental value (see e.g. Ref. [15]). An account of Coulomb- $U$  is increasing the  $M_L$  value to  $0.45 \mu_B$  [16], improving substantially the agreement with the experimental data.

In conclusion, employing correlated band theory LSDA+ $U$  calculations we have provided a microscopic picture of the anomalous enhancement of the Co-adatom orbital moment. It is found that two major effects need to be included in order to essentially improve the Co orbital moment: (i) a correct LSDA+ $U$  orbital polarization due to the Coulomb- $U$  and (ii) structural relaxation of the Co-Pt interatomic distance. The calculated value of  $M_L$  is found in fairly good agreement with experimental XMCD data [1] when those effects are taken into account.

### 3. Acknowledgments

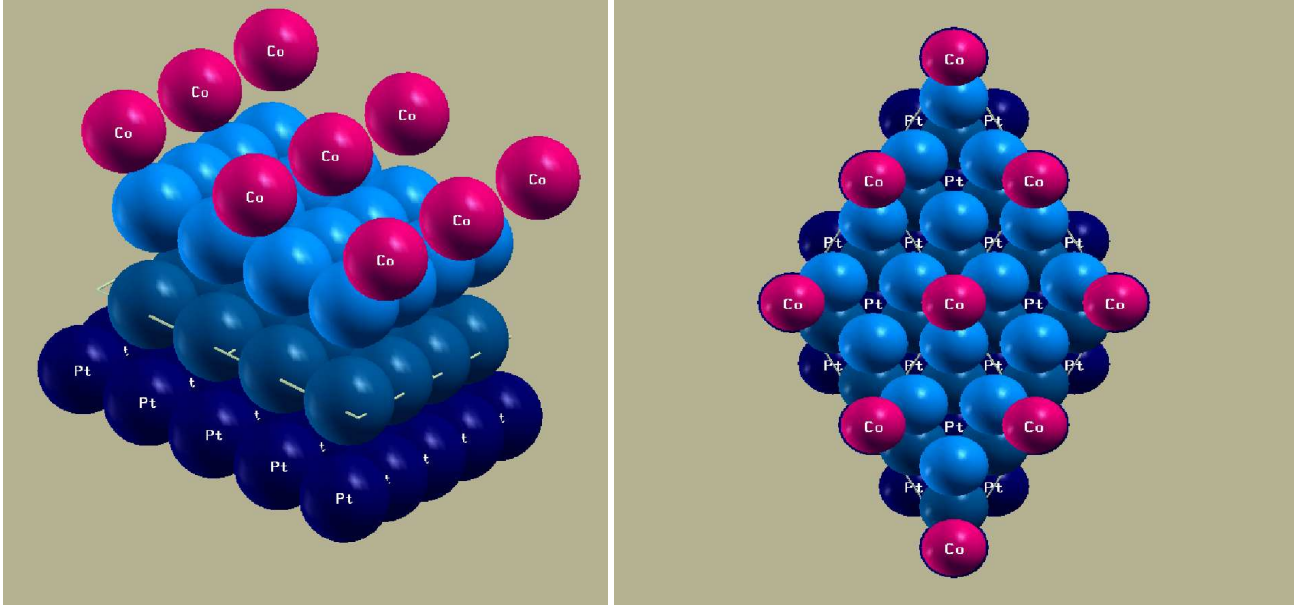
We gratefully acknowledge discussions with W. Wurth, P.M. Oppeneer, and O.N. Mryasov. Financial support was provided by the Grant Agency of the Academy of Sciences (Project A100100530), DFG Grant SFB668-A3 (Germany) and German-Czech collaboration program (Project 436TSE113/53/0-1, GACR 202/07/J047).

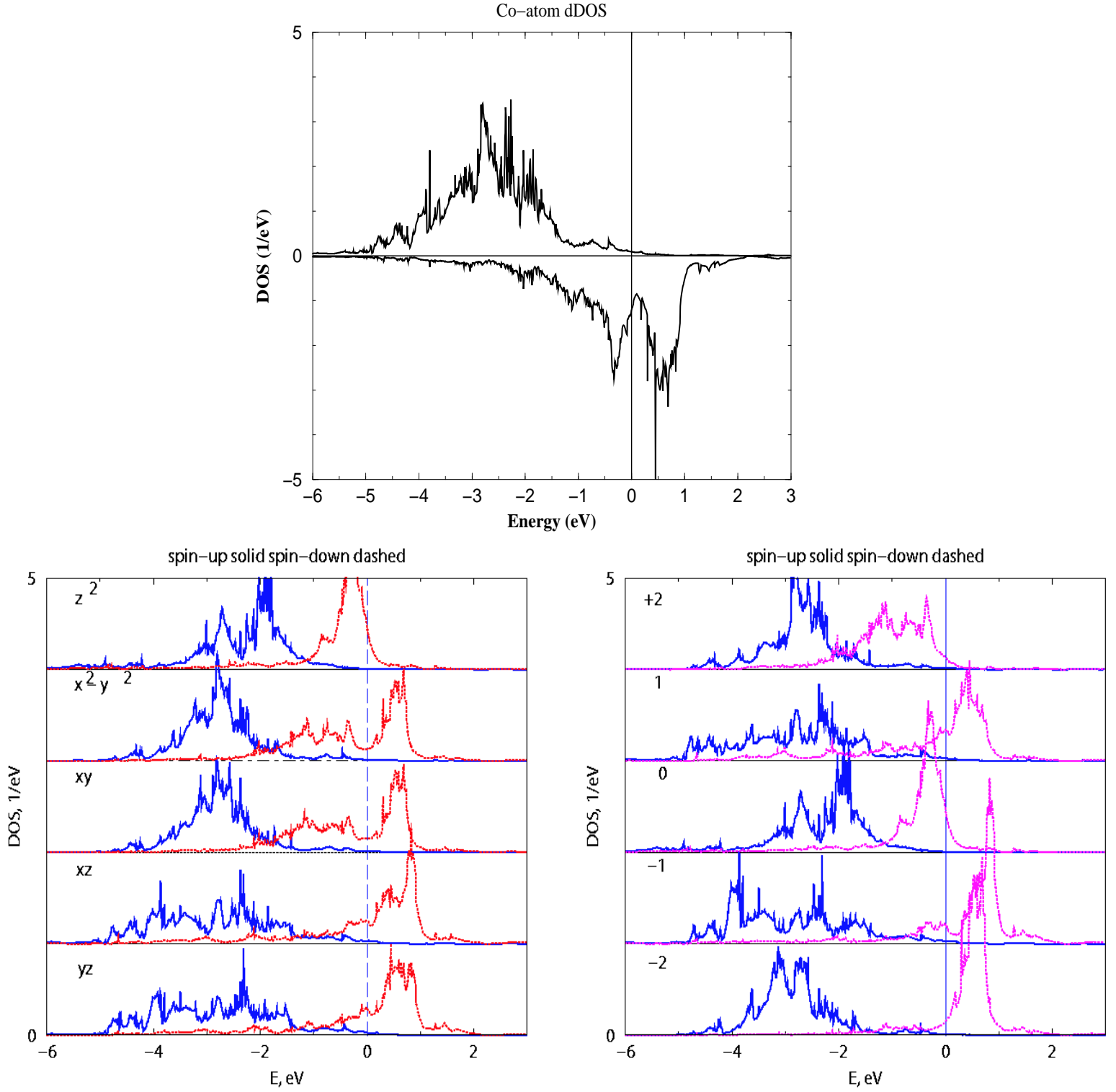
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**Table 1.** Spin ( $M_S$ ), Orbital ( $M_l$ ) magnetic moments (in  $\mu_B$ ), and Orbital moment per  $d$ -band hole ( $n_h$ ) for a Co atom on Pt(111) resulting from the LSDA and LSDA+U calculations.

Co ad-atom/Pt(111)	KKR [1]	$M_S$	$M_l$	$M_l/n_h$
LSDA		2.14	0.60	0.25
LSDA+OP/2		2.14	1.50	0.63
<b>CoPt<sub>12</sub></b>	FP-LAPW	$M_S$	$M_l$	$M_l/n_h$
LSDA		2.18	0.57	0.20
LSDA+U	$U_{Co} = 2.0$ eV, $J_{Co}=0.9$ eV			
unrelaxed	$d_{Co-Pt}=4.27$ a.u.	2.23	2.07	0.70
relaxed	$d_{Co-Pt}=3.48$ a.u.	2.14	1.58	0.54
Experiment	<b>XMCD</b> [1] $n_h = 2.4$		$1.1 \pm 0.1$	$0.46 \pm 0.04$
Experiment	<b>XMCD</b> ( $n_h = 2.92$ )		$1.34 \pm 0.12$	

**Figure 1.** Schematic crystal structure of a model super-cell: (left) general view, (right) top-view with the Co-adatom in the *fcc* position.



**Figure 2.** DOS for a Co adatom on Pt(111): (a,top) Spin-resolved Co-atom  $d$ DOS; (b,left) Co-atom  $d$ DOS resolved in cubic harmonics; (c,right) Co-atom  $d$ DOS resolved in complex harmonics.